

CERAMICS FOR MEDICINE

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CALCIUM PHOSPHATE BASED CERAMIC WITH A RESORBABLE PHASE AND LOW SINTERING TEMPERATURE

M. N. Safina,¹ T. V. Safronova,¹ and E. S. Lukin¹Translated from *Steklo i Keramika*, No. 7, pp. 19–24, July, 2007.

The use of glasses with eutectic compositions in the system $\text{CaO} - \text{P}_2\text{O}_5$ as a sintering aid and as a source of a resorbable phase for obtaining a composite biomaterial for bone implants is examined. The use of such glass has made it possible not only to lower the sintering temperature by realization of the mechanism of liquid-phase sintering but also to form a ceramic material possessing bioresorbability. The material obtained consists of calcium hydroxyapatite, vitlokite, and calcium pyrophosphate phases.

Materials based on calcium hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ are now widely used for treating traumas and defects of human bone tissue because this compound is the main mineral component of human bone tissue [1]. The advantages of such materials are that they possess a high biological compatibility, and they are nonallergenic and non-toxic. A substantial drawback of a ceramic consisting of 100% calcium hydroxyapatite (HAP) is its extremely low resorption rate (resorption is the capability of the material to dissolve gradually in the body as bone tissue forms) in contact with intertissue liquids in the body. Consequently, it is of interest to develop and use a material that initially, eliminating the bone defect, would promote intergrowth of the bone tissue and then be gradually resorbed, becoming simultaneously a source of phosphorus and calcium for restoring the patient's own bone tissue. The resorption rate of implanted material should match the bone formation rate so that the bone can fill the cavity formed in the implant. In the process, its strength must be maintained and the bone and implant must fuse together correctly. Such materials can be used not only for filling bone defects but also as a matrix for cell cultures or as a means for delivering medicine [2].

Tricalcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ (β -TCP or vitlokite), different glasses in the systems $\text{CaO} - \text{P}_2\text{O}_5 - \text{M}_2\text{O}$ and $\text{CaO} - \text{P}_2\text{O}_5 - \text{SiO}_2 - \text{M}_2\text{O}$ ($\text{M} = \text{Na, K}$), and less often rhenanite NaCaPO_4 or calcium pyrophosphate $\text{Ca}_2\text{P}_2\text{O}_7$ (CPP)

are used as the resorbable phase [3–6]. Pyrophosphate ions participate in the regulation of important biological processes and are present in many tissues in the organism, but their concentration is highest in osteoblasts. It is believed in some quarters that sintered β -TCP promotes the formation of bone cells better than does HAP [7].

The important parameters characterizing calcium phosphates are the ratio $\text{Ca} : \text{P}$ and the solubility. Calcium phosphates are soluble for ratios $\text{Ca} : \text{P} < 1.5$. In general, the lower the ratio $\text{Ca} : \text{P}$, the more “acidic” and soluble calcium phosphate is.

HAP sinters to a density close to the theoretical value in the temperature range $1200 - 1300^\circ\text{C}$. It is believed that the temperature 1300°C is the upper critical limit for sintering HAP at which its phase composition is preserved. However, this temperature depends on the sintering medium, specifically, on the partial pressure of water vapor. Increasing the water content in the sintering atmosphere stabilizes HAP at high temperatures. Existing data show that HAP with $\text{Ca} : \text{P} = 1.68 \pm 0.02$ remained stable up to 1450°C for 3 h, and increasing the temperature to 1500°C caused HAP to decompose [3]. Dehydration and decomposition of HAP strongly depend on its stoichiometry, the atmosphere, and the partial pressure of water vapor. On heating in air, starting at 700°C , HAP with $\text{Ca} : \text{P} < 1.67$ decomposes into a mixture of HAP and TCP (the polymorphic transformation β -TCP \rightarrow α -TCP occurs at 1150°C). The phase composition of HAP with $\text{Ca} : \text{P} = 1.67$ remains constant up to 1200°C , and HAP with $\text{Ca} : \text{P} > 1.67$ transforms into a mixture of HAP and CaO [8].

¹ D. I. Mendeleev Russian Chemical Engineering University, Moscow, Russia; M. V. Lomonosov Moscow State University, Moscow, Russia.

The calcination temperature can be lowered if powders obtained by chemical precipitation are used as initial materials [9]. If cold hydrostatic compaction is used at the formation stage, then the calcination temperature can be lowered to 1100°C [10]. Another method of lowering the calcination temperature of ceramic is to introduce into the initial batch low-melting additives, for example, salts or components that form eutectic melts with the main components [11].

In order for sintering to occur by the liquid-phase mechanism the glass melt must wet the surface of the particles of the main phase. Sintering in the presence of low-melting eutectics can proceed in two directions.

In the first case, the solid phase is insoluble in the liquid phase and sintering occurs as a result of surface tension forces. The amount of the liquid phase in the system must not be less than 25–30%,² and therefore if a possible change of volume as a result of a phase transition from the solid into the liquid state is excluded, then the amount of the low-melting additive introduced into the system must not be less than 25%.

In the second case sintering is a three-stage process: rearrangement of solid-phase particles, dissolution–precipitation, and formation of a solid framework. These processes are not sharply separated in time and often occur simultaneously, affecting one another. Dissolution–precipitation can be controlled by the kinetics of the chemical reaction occurring at the interface of solid and liquid phases and by diffusion of the reaction products through the boundary layer [12]. Slow cooling (together with the furnace) can promote crystallization of the melt, imparting higher mechanical characteristics to the ceramic.

The biocompatibility of the components limits the choice of systems for ceramics for bone implants. The advantages of the system CaO–P₂O₅ are the presence of several low-melting eutectics and the presence only of chemical elements that are constituents of bone tissue. CaO–P₂O₅ glasses with eutectic compositions can be used to obtain ceramic materials with low sintering temperatures.

Three low-melting glasses with eutectic compositions exist in the CaO–P₂O₅ system (Table 1) [13].

Calcium-phosphate glasses are used as components in batch to obtain a multiphase ceramic (US Patent No. 4376168) [14]. However, only limited data on the formation of the phase composition of the materials based on HAP and glasses in the binary system CaO–P₂O₅ were presented.

The objective of the present work is to obtain a ceramic material, possessing a low sintering temperature, based on HAP and additions of CaO–P₂O₅ glass with eutectic composition. To accomplish this it was necessary to study the

TABLE 1.

Glass	Weight content, %		Melting temperature, °C	Ca : P	Phases of the eutectic
	CaO	P ₂ O ₅			
1	6.3	93.7	490	0.20	P ₂ O ₅ + CaO · 2P ₂ O ₅ + liquid
2	18.9	81.1	746	0.60	CaO · 2P ₂ O ₅ + 2CaO · 3P ₂ O ₅ + liquid
3	30.3	69.7	970	1.25	α-CaO · P ₂ O ₅ + β-2CaO · P ₂ O ₅ + liquid

processes leading to phase and microstructure formation in such a ceramic.

HAP manufactured by the “Merc” company and low-melting eutectic CaO–P₂O₅ glass No. 2 (see Table 1) were used as the initial materials.

Glass No. 2 was chosen as the optimal glass for making the glasses with the compositions indicated above. The glass made was homogeneous and was easy to pour out of the crucible. After solidifying the glass was transparent and bubble-free.

Ground CaO–P₂O₅ glass was added to the initial batch. The eutectic glasses were prepared by using ultrapure grade phosphoric acid, taken with an excess of 7%, as a source of P₂O₅. Chemically pure grade CaCO₃ was used as the source of CaO. The glasses were made in corundum crucibles at 1100–1300°C in 9 h with 30 min soaking at the maximum temperature. The melt was poured onto a metal plate which was degreased with acetone. The glass obtained was ground in an agate mortar and then in a planetary mill by the dry method.

Properties of the glass obtained

Density, g/cm ³	2.53
Open porosity, %	0
Flexural strength, MPa	60
CLTE at 650–950°C, 10 ⁻⁷ K ⁻¹	173

It is supposed that HAP in ceramic will be a source of a resistive phase. Petrographic analysis of the initial hydroxyapatite showed that the HAP powder consists of a single phase and the particles are 1–2 μm in size. The refractive index is 1.644–1.681.

The interaction of glass No. 2 with HAP was studied first. For this, samples were compacted (under pressure 50 MPa) into 4 mm high pellets of glass No. 2 and 8 and 16 mm in diameter HAP pellets, respectively. Next, a glass pellet was placed on a HAP sample and heated to 850°C at 2 K/min. The degree of the interaction between HAP and glass was evaluated every 50°C (visually, and then by petrographic analysis).

These studies showed that on heating to 850°C glass completely wets almost the entire surface of the HAP. Petrographic analysis showed that not only did glass wet the HAP surface but the glass interacted with HAP. The onset of crystallization attested to this interaction. The glass phase

² Here and below — the weight content.

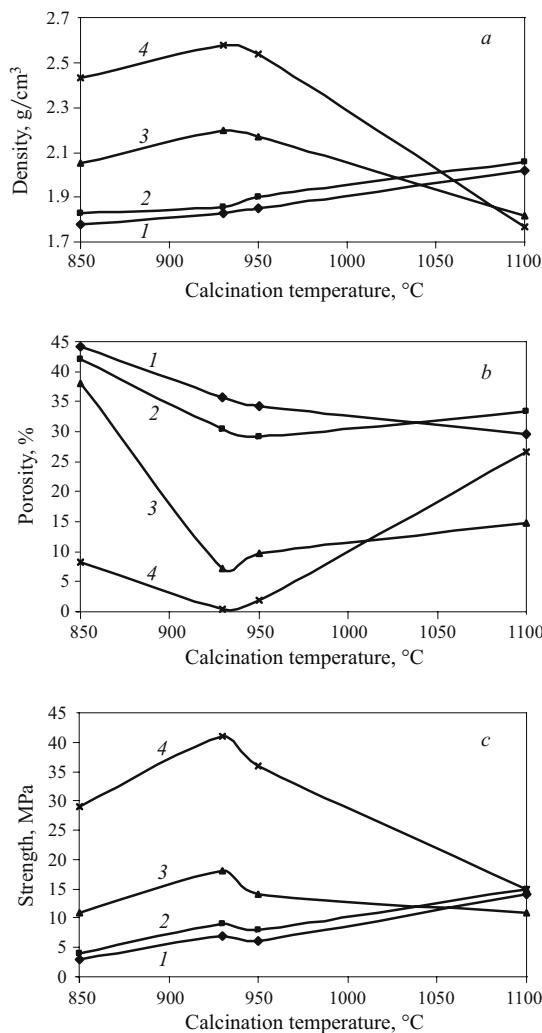


Fig. 1. Average density (a), open porosity (b), and flexural strength (c) of HAP-based samples versus the calcination temperature: 1, 2, 3, and 4) 10, 20, 30, and 40% added glass, respectively.

was distributed in the form of continuous 3.5–7.0 µm thick interlayers. The formation of secondary HAP from glass in 1–3 µm interlayers was observed. This fraction did not exceed 2%.

Comparing the CLTEs of HAP ($138 \times 10^{-7} \text{ K}^{-1}$) and glass No. 2 ($173 \times 10^{-7} \text{ K}^{-1}$) suggests that it could be pos-

sible to make a composite two-phase material based on these components. Considering the strength characteristics of the components, the use of glass as a source of a second phase should make the material stronger.

The compositions presented in Table 2 were used to make ceramic.

The samples for making HAP-based ceramic were compacted under pressure 100 MPa into $40 \times 6 \times 3$ mm rods. A solution of rubber in benzene served as temporary process binder.

The samples were calcined in the temperature range 850–1100°C with 1 h soaking at the maximum temperature (heating rate 3 K/min) and samples based on pure HAP were calcined at 1200°C with 2 h soaking at the maximum temperature.

Properties of HAP-based ceramic samples without additives

Density, g/cm ³	2.74
Open porosity, %	16.9
Flexural strength, MPa	38
CLTE at 650–950°C, 10^{-7} K^{-1}	138

The main properties of the samples were determined after calcination.

The average density of the samples with 10, 20, 30, and 40% addition of glass is 1.77–2.58 g/cm³, the open porosity is 0.5–44.1%, and the flexural strength is 6–41 MPa. As the glass content increases from 10 to 40%, the average density and flexural strength increase and the open porosity decreases (Fig. 1).

For the compositions with 10 and 20% glass No. 2, as the calcination temperature increases in the range 850–1100°C the average density increases from 1.78 to 2.02 and from 1.83 to 2.06 g/cm³, the mechanical strength increases from 3 to 14 and from 4 to 15 MPa, and the open porosity decreases from 44.1 to 29.5 and from 42.0 to 33.4%, respectively. The density of the samples with 30 and 40% added glass increases and reaches the maximum value at 930°C, equal to 2.20 and 2.58 g/cm³, after which it decreases to 1.82 and 1.77 g/cm³, respectively.

For compositions with 30 and 40% added glass, the behavior of the flexural strength is similar to the dependence of the average density on the calcination temperature. The maximum strength of these compositions (18 and 41 MPa) is observed at 930°C; as temperature increases further, the strength decreases to 11 and 15 MPa, respectively (at 1100°C). The minimum value of the open porosity for these samples (7.1 and 0.5%) is observed at 930°C, and as temperature increases further the porosity increases.

The calcination temperature 930°C for compositions with 30 and 40% glass is critical. Above this temperature the density decreases and the mechanical properties degrade as a result of phase transformations in the material.

TABLE 2.

Batch	Weight content, %	
	glass No. 2	HAP
1	10	90
2	20	80
3	30	70
4	40	60
5	0	100

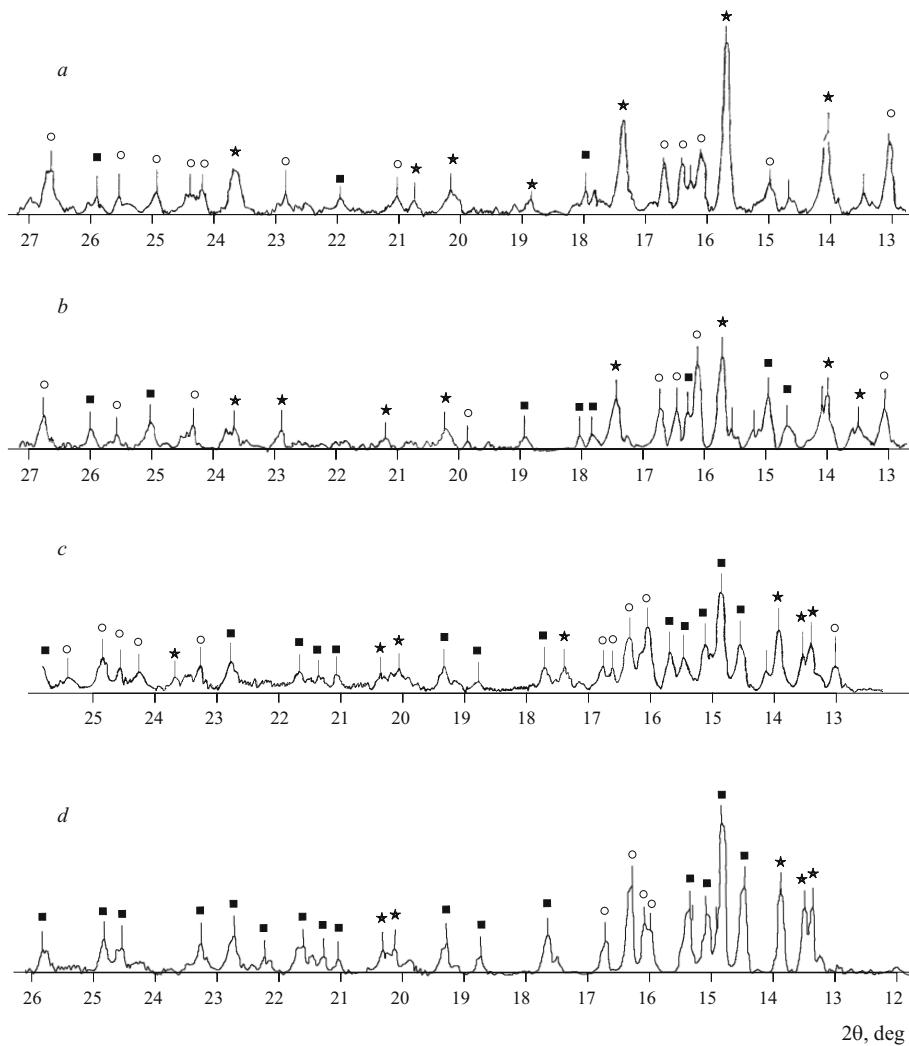


Fig. 2. X-ray diffraction patterns of ceramic samples, calcined at 930°C and soaked for 1 h, based on HAP with No. 2 glass added in the amounts 10 (a), 20 (b), 30 (c), and 40% (d). ○ HAP; ★) β-TCP; ■) β-CPP.

The samples with 40% glass which were calcined at 930°C possessed the best characteristics compared with samples with different compositions — average density 2.58 g/cm³, open porosity 0.5%, and flexural strength 41 MPa.

After calcination the samples with different glass content (see Table 2) were analyzed by x-ray phase, IR-spectral, and petrographic methods. The calcined samples based on pure HAP were evaluated only by petrographic analysis.

The x-ray diffraction patterns of the ceramic calcined at 930°C are presented in Fig. 2.

Each composition contains HAP ($d = 3.440$, 2.817, 2.779, and 2.723 Å). In addition to the peaks due to HAP, as the amount of added glass increases, peaks due to new crystalline compounds appear. These peaks correspond to β-tricalcium phosphate or vitrokite $\beta\text{-Ca}_3(\text{PO}_4)_2$ — β-TCP

($d = 3.450$, 3.2120, 2.880, and 2.607 Å) and β-calcium pyrophosphate $\text{Ca}_2\text{P}_2\text{O}_7$ — β-CPP ($d = 8.010$, 6.950, 3.420, and 3.210 Å). The peaks due to β-TCP and β-CPP increase in intensity as more additive is added. This indicates that these components form as a result of the interaction of glass and the main phase as well as by crystallization from glass.

The IR spectra of the calcined samples (Fig. 3) differ substantially from the spectra of the uncalcined pure HAP powder. In the first place, the wide absorption bands of groups in the region $3600 - 2600 \text{ cm}^{-1}$, which are present in the IR spectra of HAP, are absent in these IR spectra. In the second place, the bands characterizing the stretching and flexural vibrations of the PO_4 groups are split into components. The stretching vibrations of these groups lie in a wider range — $900 - 1200 \text{ cm}^{-1}$, and the flexural vibrations lie in the range $450 - 600 \text{ cm}^{-1}$.

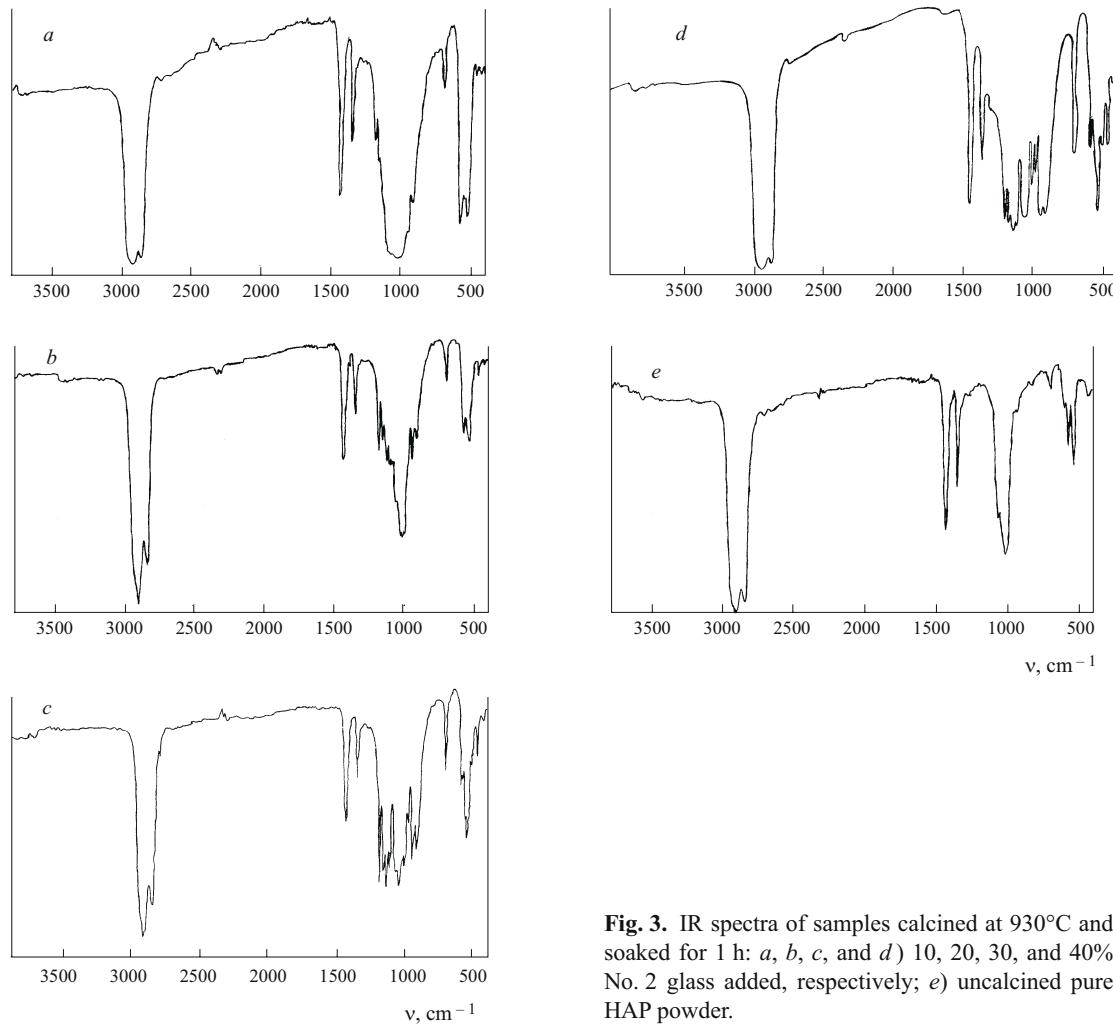


Fig. 3. IR spectra of samples calcined at 930°C and soaked for 1 h: *a*, *b*, *c*, and *d*) 10, 20, 30, and 40% No. 2 glass added, respectively; *e*) uncalcined pure HAP powder.

The IR spectrum of the composition No. 1 (10% added glass) is similar to that of β -TCP, which agrees with XPA — the composition is a mixture of HAP and β -TCP. A large number of narrow absorption bands appear in the IR spectra of the compositions Nos. 2 (20% glass) and 3 (30% glass) together with absorption bands characterizing β -TCP in the region of the stretching and flexural vibrations of the PO_4 groups. For example, the wide absorption band of PO_4 groups, which is present in the IR spectrum of the composition No. 2 (20% glass), with a maximum at 1020 cm^{-1} is the strongest band. Four narrow absorption bands of average intensity appear on the high-frequency side in the region $1100 - 1200\text{ cm}^{-1}$ and two bands of average intensity and an inflection at 980 cm^{-1} are recorded on the low-frequency side in the region $900 - 1000\text{ cm}^{-1}$. In the IR spectrum of composition No. 3 (30% glass) the intensity of the absorption band in the regions $900 - 1000$, $1000 - 1100$, and $1100 - 1200\text{ cm}^{-1}$ is essentially flat. The intensity of the 720 cm^{-1} band changes. In the IR spectrum of composition No. 4 (40% glass) the intensity of the absorption bands changes further in the region of the flexural and stretching

vibrations of the PO_4 groups. The IR spectrum differs substantially from the preceding spectra. It corresponds to the spectrum of β -CPP. As the amount of glass increases (compositions Nos. 2 – 4) the content of the β -CPP phase also increases.

Petrographic analysis established that the main crystalline phases in the calcined materials were also HAP ($1 - 5\text{ }\mu\text{m}$ grains), β -TCP (particle size $2 - 4\text{ }\mu\text{m}$), and β -CPP (grain size $2 - 5\text{ }\mu\text{m}$). The β -CPP phase was not found in the ceramic with the composition No. 1 (10% glass). As the glass content increases, the fraction of TCP and CPP, whose crystals are close in size, also increases. Closed intercristalline porosity in the form of clusters of pores, ranging in size from 6 to $15\text{ }\mu\text{m}$, present in amounts up to 15% is observed in the calcined samples. A salient feature of the microstructure of the samples is that the β -TCP and β -CPP phases crystallize in the form of a solid solution along the boundaries of HAP crystals.

According to the phase diagram the final phases of the crystallization of glass No. 2 with eutectic composition (see Table 1) are calcium ultra- and metaphosphate. However, the

glass composition can shift during founding and sintering as a result of the high volatility of phosphorus oxide, even though a 7% excess was taken to prepare the glass. The formation of β -TCP is possible in the material as a result of the thermal decomposition of HAP and as a result of the interaction of the β -CPP phase and HAP [6].

The ceramic based on pure HAP contained after calcination a small amount of the β -TCP phase (5–7%). The grain size of the isometric form of the main phase HAP was 3–6 μm . The second phase, β -TCP, in form of crystals up to 2 μm in size was distributed along the periphery of the grains of the main phase. Closed intercrystalline porosity (pore size 2–3 μm) up to 4% was observed in the material.

Adding $\text{CaO} - \text{P}_2\text{O}_5$ glass with eutectic composition when HAP-based material is obtained not only decreased the sintering temperature to 930°C as result of the realization of the liquid-phase sintering mechanism but it also resulted in the formation of ceramic material which will possess enhanced bioresorbability because of the presence of the β -TCP and β -CPP phases.

The composite biomaterial obtained (flexural strength 40 MPa, average density 2.58 g/cm³, and open porosity 0.5%) can be recommended for tests under clinical conditions.

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